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A Facile Synthesis of Stable Heterocyclic Phosphorus Ylides

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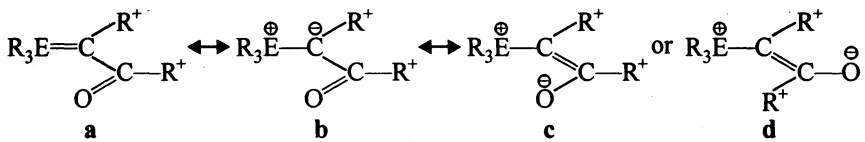
Stable crystalline phosphorus ylides are obtained from the 1 : 1 : 1 addition between tertiary phosphine, dialkyl acetylenedicarboxylate and strong N—H acids, such as imidazole or benzimidazole. These compounds were identified by FTIR, FTNMR and elemental analysis.

Key Words: Synthesis, Phosphorus ylides.

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis[1–7]. The keto-stabilized phosphorus ylide $R_3P{=}CRCOR'$ ($R = CHZCO_2Me$ and $R' = OMe$) have been found to be an interesting ligand in organometallic chemistry and a useful intermediate for organic synthesis[8]. Keto phosphorus ylides such as $Ph_3P{=}CRCOR'$ represent key ligands for the formation of phosphino enolate metal complexes, a class of compounds of growing importance. The ylide $R_3P{=}CRCOR'$ offers new synthetic possibilities, in addition to the known C— and O— coordination (**Scheme 1**) as has been suggested[9]:

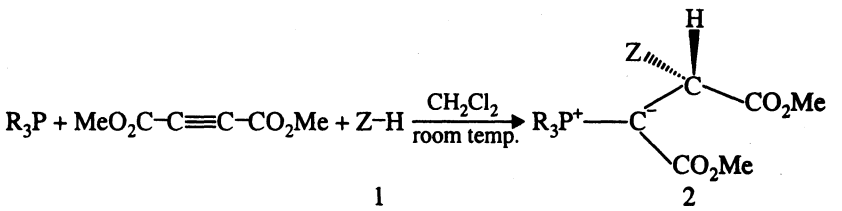


Scheme-1

RESULTS AND DISCUSSION

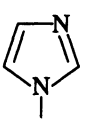
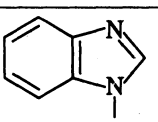
Several methods have been developed for preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base where phosphonium salts are usually prepared from the phosphine and alkyl halide[1, 2]. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins among other methods[1]. These salts are most often converted to the ylide by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. An efficient synthetic route to stable phosphorus ylides using triphenylphosphine and chlorodiphenylphosphine, dimethyl acetylenedicarboxylate and heterocyclic ZH-acids, such as imidazole or benzimidazole has been reported. Thus, reaction of ZH-acids **1** with di-methyl acetylene-dicarboxylate in the presence of tertiary phosphines leads to the

corresponding stable heterocyclic phosphorus ylides **2** in excellent yields (**Scheme-2**, Table-1):

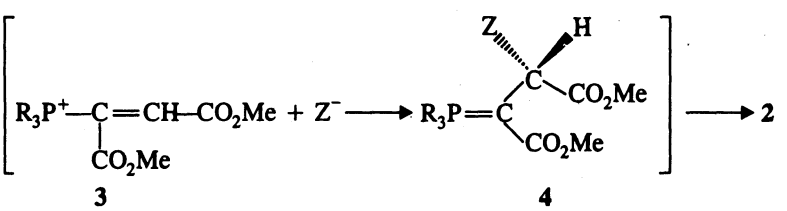


Scheme-2

TABLE-1
STABLE HETEROCYCLIC PHOSPHORUS YLIDES **2**

2	R	Z	Yield of 2 (%)
a	*p*-$(C_6H_5)_3$		85
b	*p*-$(C_6H_5)_2Cl$		80
c	*p*-(*p*-$MeC_6H_4)_3$		81
d	*p*-$(C_6H_5)_3$		79
e	*p*-$(C_6H_5)_2Cl$		82

On the basis of the well established chemistry of trivalent phosphorus nucleophiles[1-7] it is reasonable to assume that phosphorus ylide **2** results from the initial addition of trivalent phosphorus (triphenylphosphine, chlorodiphenyl-phosphine and *p*-tolylphosphine) to the acetylenic ester and subsequent protonation of the 1 : 1 adduct by the NH-acid. Then, the positively charged ion **3** is attacked by the anion of the NH-acid (Z^-) to form phosphorane **4** which apparently isomerizes, under the reaction conditions, to produce the compound **2** (**Scheme-3**).



Scheme-3

The following advantages have been suggested for this route:

1. Heterocyclic phosphorus ylides above are new compounds in organometallic for catalytic purpose.
2. The preparation of phosphorus ylides in this route is easy and simple.
3. Heterocyclic phosphorus ylides above are stable for time under atmospheric condition.

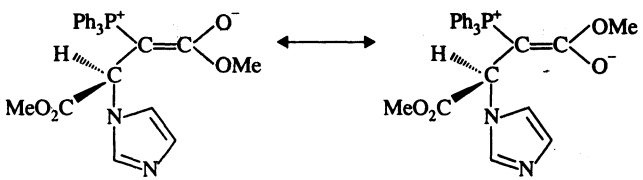
4. These compounds are useful intermediates for preparation of cycloalkene derivatives.

EXPERIMENTAL

IR and NMR spectra were recorded by using an FT-IR spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer respectively. NMR chemical shifts were measured relative to TMS (int; ^1H) and 85% H_3PO_4 (int; ^{31}P).

Preparation of dimethyl-2-(imidazole-1-yl)-3-(chloro diphenylphosphoranylidene)butanedioate (2a): In a 50 mL round-bottomed flask to a magnetically stirred solution of imidazole (0.136 g, 2 mmol) and chlorodiphenyl phosphine (0.441 g, 2 mmol) in CH_2Cl_2 (15 mL) was added, dropwise, a mixture of di-methyl acetylenedicarbo-xylate (0.452 g, 2 mmol) in CH_2Cl_2 (5 mL) at −10°C for 10 min. The reaction mixture was then allowed to warm up to room temperature and stand for 30 h. The solvent was removed under reduced pressure and the solid residue was washed by cold diethyl ether (2 × 5 mL) and the product **2b** was obtained as dark brown powder (0.823 g, 80%), m.p. 158–160°C. IR (KBr) (ν_{max}, cm^{-1}): 1727.5 ν(C=O); 1590 ν(C=C); 899 ν(P—C). ^1H-NMR ($CDCl_3$) δ = 2.26 (6H, s, $2CH_3$), 3.67 (1 H, d, $CHCO_2Me$), 6.8 (1 H, br s, CH), 7.17 (1H, br s, CH), 7.4–8 (10 H, m, $2C_6H_5$), 9.45 (1H, br s, CH). ^{31}P-NMR δ = 27.06 (s). (Found: C, 58.76; H, 4.42; N, 6.52; Calcd. for $C_{21}H_{20}N_2PO_4Cl$: C, 58.56; H, 4.68; N, 6.50%).

Dimethyl-2-(imidazole-1-yl)-3-(triphenylphosphoranylidene)butanedioate (2b): The yellow powder (m.p. 123–125°C, yield 0.473 g or 85%). IR (KBr) (ν_{max}, cm^{-1}): 1721 ν(C=O); 1641 ν(C=C); 1305 ν(C—N); 887 ν(C—P). ^1H-NMR ($CDCl_3$) δ = 3.19, 3.65 (6H, s, $2CH_3$, minor isomer), 3.79 (6H, s, $2CH_3$, major isomer), 3.90 (1H, d, $^3J_{HP}$ 15.42 Hz, $CHCO_2Me$, minor isomer), 4.49 (1H, d, $^3J_{HP}$ 15.57 Hz, $CHCO_2Me$, major isomer), 6.86 (1H, d, $^3J_{HH}$ 16.47 Hz, CH), 7.04 (1H, d, $^3J_{HH}$ 16.5 Hz, CH), 7.2–8 (15H, m, $3C_6H_5$), ^{31}P-NMR δ = 26.81 (s, major isomer), δ = 21.45 (s, minor isomer). (Found: C, 68.39; H, 5.22; N, 5.93; Calcd. for $C_{27}H_{25}N_2PO_4$: C, 68.66; H, 5.22; N, 5.93%) **(Scheme 4):**



Scheme 4. Major and minor isomer (**2b**)

Dimethyl-2-(imidazole-1-yl)-3-(triparatolylphosphoranylide) butanedioate (2c): The brown light powder (m.p. 96–98°C, yield 0.417 g or 81%). IR (KBr) (ν_{max}, cm^{-1}): 1739 ν(C=O); 1600 ν(C=C); 1308 ν(C—N); 889 ν(C—P). ^1H-NMR ($CDCl_3$) δ = 1.25, (6H, m, $2CH_3$), 2.3 (9H, m, $3CH_3$), 3.80 (1H, br, $CHCO_2Me$), 7.15 (1H, s, CH), 7.27 (1H, br, CH), 7.40–8 (13H, m, $3C_6H_4$, 1CH), ^{31}P-NMR δ = 26.71 (s). (Found: C, 70.03; H, 6.51; N, 5.37; Calcd. for $C_{30}H_{31}N_2PO_4$: C, 71.06; H, 6.03; N, 5.44%).

Dimethyl-2-(benzimidazole-1-yl)-3-(triphenylphosphoranylidene)butanedioate (2d): The yellow powder (m.p. 143–145°C, yield 0.413 g or 79%). IR (KBr) (ν_{max}, cm^{-1}): 1729 ν(C=O); 1610 ν(C=C); 1309 ν(C—N); 887 ν(C—P). ^{1}H-NMR δ = 3.81, (6H, s, $2CH_3$), 6.07 (1H, d, $^3J_{HP}$ 12 Hz, $CHCO_2Me$), 6.86–8.09 (19H, m, $3C_6H_5$, $1C_6H_4$), 8.61 (1H, CH—N). ^{31}P-NMR δ = 27.28 (s). (Found: C, 70.55; H, 5.36; N, 5.39; Calcd. for $C_{31}H_{27}N_2PO_4$: C, 71.25; H, 5.21; N, 5.36%).

Dimethyl-2-(benzimidazole-1-yl)-3-(chlorodiphenylphosphoranylidene) butanedioate (2e): The dark brown powder (m p. 178–181°C, yield 0.394 g or 82%). IR (KBr) (ν_{max}, cm^{-1}): 1731 ν(C=O); 1618 ν(C=C); 1302 ν(C—N); 885 ν(C—P). ^{1}H-NMR ($CDCl_3$) δ = 1.09, (3H, s, CH_3), 1.20 (3H, s, CH_3), 3.56 (1H, d, $^3J_{HP}$ 18.7 Hz, $CHCO_2Me$), 6.2–8 (14H, m, $2C_6H_5$, $1C_6H_4$), 10.11 (1H, s, CH—N). ^{31}P-NMR δ = 31.19 (s). (Found: C, 62.50; H, 4.90; N, 5.81; Calcd. for $C_{25}H_{22}N_2PO_4Cl$: C, 62.45; H, 4.61; N, 5.82%).

REFERENCES

1. D.E.C. Cobridge, Phosphorus: An Outline of the Chemistry, Biochemistry and Uses, 5th Edn., Elsevier, Amsterdam (1995).
2. R. Engel, Synthesis of Carbon-Phosphorus Bonds, CRC Press, Boca Raton, Florida (1988); J.I.G. Cadogen, Organophosphorus Reagents in Organic Synthesis, Academic Press, New York (1979).
3. O.I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66**, 225 (1997).
4. H.J. Bestmann and R. Zimmermann, *Top. Curr. Chem.*, **20**, 88 (1971); H.J. Bestmann and O. Vostrosky, *Top. Curr. Chem.*, **109**, 85 (1983).
5. B.E. Maryano and A.B. Reitz, *Chem. Rev.*, **89**, 863 (1989).
6. K.M. Pietrusiewiz and M. Zablocka, *Chem. Rev.*, **94**, 1375 (1994).
7. R.A. Aitken, H. Herion, A. Janosi, N. Karodia, S.V.S. Raut, S. Seth, I.J. Shannon and F.C. Smith, *J. Chem. Soc. Perkin Trans.*, **1**, 2467 (1994).
8. J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc. Dalton Trans.*, 2579 (1991) and refs. therein.
9. U. Belluco, R.A. Michelin, M. Mozzon, R. Bertani, G. Facchin, L. Zanotto and L. Pandolfo, *J. Organomet. Chem.*, **557**, 37 (1998).

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